

Claims

1. A process of manufacturing a metal sheet precoated with an antimicrobial polymer coating, comprising:
- providing a metal sheet substrate having two opposed planar surfaces comprising a base metal selected from the group consisting of aluminum, iron, nickel, titanium, molybdenum, magnesium, manganese, copper, silver, lead, tin, chromium, beryllium, tungsten, cobalt and alloys thereof;
- cleaning the surface of the substrate wherein cleaning comprises removing bulk and molecular organic contaminants;
- pretreating at least one planar surface of the substrate to promote adhesion of a polymer coating;
- applying a polymer coating onto at least one planar surface of the substrate by roll coating the substrate with a polymer containing an anti-microbial powder comprising core particles associated with an antimicrobial metal component;
- wherein the content of the antibiotic powder is in the range of from about 0.2 to about 30 weight percent of the polymeric coating;
- wherein the core particle is an oxide selected from the group consisting of titanium, aluminum, zinc and copper, sulfates of calcium, strontium and barium, zinc sulfide, copper sulfide, zeolites, zirconium phosphate, mica, talc, kaolin, mullite, silica and mixtures thereof;
- wherein the antimicrobial metal component is selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions and mixtures thereof; and
- treating the coated substrate to produce at least a partially hardened and adhered antimicrobial coating on the final sheet product.

2. The process of claim 1 wherein the base metal is a metal selected from the group consisting of steel, zinc, iron, aluminum, copper and mixtures thereof.
3. The process of claim 2 wherein the metal sheet is provided as a continuous strip.
4. The process of claim 3 wherein the base metal is a nickel alloy selected from the group consisting of steel, zinc, zinc based alloys, zinc coated steel, zinc aluminum alloy coated steel, aluminum and aluminum alloy.
5. The process of claim 3 wherein the base metal is a nickel alloy selected from the group consisting of nickel manganese, nickel-aluminum, nickel silver, nickel bronze and nickel-silicon.
6. The process of claim 3 wherein the base metal is a copper alloy such as brass, bronze, silicon bronze, silicon brass, nickel silver and nickel bronze
7. The process of claim 3 wherein the base metal is an aluminum-based metal selected from the group consisting of pure aluminum, aluminum oxide, and aluminum alloy.
8. The process of claim 7 wherein the base metal is an aluminum alloy selected from the group consisting of Al-C<sub>1</sub>, Al-Mg, Al-Si, Al-Cu-Ni-Mg and Al-Si-Cu-Ni-Mg.
9. The process of claim 3 wherein the base metal is an iron-based metal selected from the group consisting of pure iron, iron oxide, carbon steel, Ni steel, Cr steel, Ni-Cr steel, Cr-Mo steel, Ni-Cr-Mo steel, stainless steel, silicon steel, Permalloy, non-magnetic steel, magnetic steel, and cast steel.
10. The process of claim 3 wherein the base metal is an alloy steel selected from the group consisting of carbon steel, Ni steel, Cr steel, Ni-Cr steel, Cr-Mo steel, stainless steel, silicon steel and Permalloy.
11. The process of claim 3 wherein the base metal is galvanized steel.

12. The process of claim 3 wherein the cleaning step comprises a cleaning method selected from the group consisting of solvent cleaning, emulsion cleaning, alkaline cleaning, acid cleaning, pickling, salt bath descaling ultrasonic cleaning, and combinations thereof.
13. The process of claim 12 wherein the cleaning step is by alkaline cleaning with an alkaline solution comprising one or more agents selected from the group consisting of caustic soda, soda ash, alkaline silicates, sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates, alkaline builders, ammonium acid phosphate, ammonium hydroxide, monoethanol amine, and dimethylamine oxide.
14. The process of claim 13 wherein the alkaline solution additionally contains one or more of the agents selected from the group consisting of complexing agents, surfactants, sequestrant, builders, surface-active agents, defoaming agents, and mixtures thereof.
15. The process of claim 14 wherein the alkaline builder comprises one or more of the agents selected from the group consisting of sodium silicate, trisodium phosphate, caustic soda, disodium phosphate, sodium pyrophosphate, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, and sodium sesquicarbonate.
16. The process of claim 13 wherein the temperature of the alkaline solution is between about 25° and about 95°C.
17. The process of claim 12 wherein the metal surface having been contacted by the cleaning solution is rinsed with water.
18. The process of claim 17 wherein the rinsing is followed by drying.

19. The process of claim 13 wherein the pretreating creates a chemical conversion interlayer coating selected from the group consisting of a silane, phosphate, chromate, epoxy, oxide, adhesive and mixtures thereof.
20. The process of claim 19 wherein the interlayer is formed by contacting the metal with a composition selected from the group consisting of chromium phosphate, chromium chromate, zinc phosphate, iron phosphate, or an epoxy.
21. The process of claim 20 wherein the interlayer is formed by contacting the metal with an aqueous phosphating composition comprising phosphoric acid and a divalent metal ion wherein the composition has total phosphate content from about 0.01 to about 3 moles/liter and the metal ion is selected from the group consisting of divalent transition metal ions and alkaline earth divalent metal ions.
- 5 22. The process of claim 21 wherein the divalent metal ion is selected from the group consisting of Mn, Co, Fe, Ni, and Zn.
23. The process of claim 21 wherein the divalent metal ion is selected from the group consisting of Mg, Ca, Sr, and Ba.
24. The process of claim 21 wherein the divalent metal ion is selected from the group consisting of Fe, Ni and Zn.
25. The process of claim 24 wherein the phosphating composition additionally comprises an oxidant is selected from the group consisting of bromate, chlorate, nitrate, nitrite, organic nitro compounds, perborate, persulfate or hydrogen peroxide, m-nitrobenzene sulfonate, nitrophenol and combinations thereof.
- 5 {6 26. The process of claim 24 wherein the phosphating composition additionally comprises one or more compounds selected from the group consisting of sulfate, fluoride, silicofluoride, boron fluoride, citrate, tartrate, hydroxy-carboxylic acids, aminocarboxylic acids, condensed phosphates, silicates, alkali metal metasilicate, alkali metal orthosilicate, and alkali metal disilicate.

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27. The process of claim 24 wherein the phosphating composition additionally comprises silicate.
28. The process of claim 21 wherein the metal substrate is predominantly aluminum and wherein the phosphating composition includes an activator present as fluoride ions in amounts up to 1.0 moles/liter.
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30. The process of claim 21 wherein the metal substrate is predominantly galvanized steel or steel and wherein the phosphating composition includes boric acid in an amount of at least 0.02.
30. The process of claim 24 wherein the interlayer is between about 0.01 to about 30 microns thick.
31. The process of claim 24 wherein the interlayer is at least partially dried by heating.
32. The process of claim 31 wherein the drying temperature is between about 25° and about 95°C.
33. The process of claim 31 wherein the drying temperature is from at least 50°C.
34. The process of claim 13 wherein the polymer is an organic polymer material selected from the group consisting of acetate rayon, acrylic resins, acrylonitrile-butadiene-styrene resins and acrylic resins, aliphatic and aromatic polyamides, aliphatic and aromatic polyesters, allyl resins, butadiene resins, chlorinated polyethylene, conductive resins, copolymerised polyamides, copolymers of ethylene and vinyl acetate, cuprammonium rayons and natural and synthetic rubbers, EEA resins, epoxy resins, ether ketone resins, ethylene vinyl alcohol, fluorine resins, fluorocarbon polymers, fluoroplastics, high density polyethylenes, ionomer resins, liquid crystal polymer, low density polyethylenes, melamine formaldehyde, natural polymers such as cellulosics, nylons, phenol-formaldehyde plastic, phenolic resins, polyacetal, polyacrylates, polyacrylonitrile, polyamide, polyamide-imide, polyaryletherketone, polybutadiene, polybutylene terephthalate, polybutylene,

polycarbonate, polycarbonates, polydicyclopentadiene, polyketones, polyester  
15 block copolymers, polyesters, polyesterurethane, polyesterurethaneurea,  
polyether and polyester block polymers, polyether ketoneketone  
polyetherether ketone polyetherimide, polyethers, polyethersulfone,  
polyetherurethane, polyetherurethaneurea, polyethylene isophthalate,  
polyethylene terephthalate, polyethylene, polyethylenechlorinates,  
20 polyglycolic acid, polyhexamethylene terephthalate, polyimide, polylactic  
acid, polymethylpentene, poly-m-phenylene isophthalamide, polyolefins,  
polyphenylene oxide, polyphenylene sulfide, polyphthalamide, poly-p-  
phenylene terephthalamide, polypropylene, polysiloxanes, polystyrene,  
polysulfides, polysulfone, polytetrafluoroethylene, polyurethane, polyvinyl  
acetate, polyvinyl alcohols, polyvinylchloride, polyvinylidene chloride,  
25 polyvinylidene fluoride and polyvinyl fluoride, rayon, reconstituted silk and  
polysaccharides, reinforced polyethylene terephthalate resins, segmented  
polyurethane elastomers, silicone resins, elastane elastomers, styrene-type  
specific resins, thermoplastic polyurethane elastomers, phenol-formaldehyde  
30 copolymer, triacetate rayon, unsaturated polyester resins, urea resins, urethane  
resins, vinyl chloride resins, vinyl polymers, vinylidene chloride resins and  
copolymers, terpolymers and mixtures thereof.

35. The process of claim 20 wherein the polymer is selected from the group  
consisting of acrylic resins, polyester resins, polyethylene, polypropylene,  
epoxy resins, polyurethane resins, olefin resins, polyamide resins, ethylene-  
vinyl acetate copolymer, ethylene-vinyl alcohol copolymer, polyvinyl  
chloride, polyvinylidene chloride, polystyrene, ABS resin, polyethylene  
5 terephthalate, nylon, polycarbonate and copolymers, terpolymers and mixtures  
thereof.
36. The process of claim 20 wherein the polymer is selected from the group  
consisting of aminoalkyd resins, aminoacrylic resins, polyvinyl chloride and  
polyesters.
37. The process of claim 20 wherein the polymer is a polyester.

38. The process of claim 20 wherein the polymer is an epoxy selected from the group consisting of phenolic-modified epoxies, polyester-modified epoxies, epoxy-modified polyvinyl chloride, and cross linkable epoxies.
39. The process of claim 20 wherein the polymer is an epoxy.
40. The process of claim 35 wherein the core particle is a natural zeolite selected from the group consisting of analcime, chabazite, clinoptilolite, erionite, faujasite, mordenite, and phillipsite.
41. The process of claim 35 wherein the core particle is a synthetic zeolite selected from the group consisting of A-type zeolite, X-type zeolite, Y-type zeolite, and mordenite.
42. The process of claim 41 wherein the core particle is a synthetic zeolite whose ion-exchangeable ions are partially or completely ion-exchanged with antibiotic metal ions.
43. The process of claim 42 wherein the ion-exchangeable ions are selected from the group consisting of sodium ions, potassium ions, calcium ions, magnesium ions and iron ions and wherein the antibacterial metals ions are selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions or mixtures thereof, and wherein the zeolite particles retain the antibacterial metal ions at ionic exchange sites of the zeolite in an amount less than the ion exchange saturation capacity of the zeolite.
44. The process of claim 43 wherein the zeolite is ion-exchanged with metal ions in an amount less than about 90% of the ion-exchangeable saturation capacity of the zeolite particles.
45. The process of claim 44 wherein the antibacterial metals ions are selected from the group consisting of silver, copper or zinc ions or mixtures thereof.
46. The process of claim 44 wherein the antibacterial metal ions are silver.

47. The process of claim 45 wherein additional metal ions selected from the group consisting of sodium, potassium, magnesium, calcium, aluminum, titanium, cerium and ammonium ion co-exist on the zeolite.
48. The process of claim 44 wherein the amount of antimicrobial component on the core particle is at least about 0.1% by weight, based on anhydrous zeolite plus metal.
49. The process of claim 44 wherein the amount of antimicrobial component on the core particle is at least about 0.2% by weight, based on anhydrous zeolite plus metal.
50. The process of claim 44 wherein the amount of antimicrobial component on the core particle is at most about 20% by weight, based on anhydrous zeolite plus metal.
51. The process of claim 44 wherein the amount of antimicrobial component on the core particle is at most about 15% by weight, based on anhydrous zeolite plus metal.
52. The process of claim 44 wherein the amount of antimicrobial component on the core particle is at most about 10% by weight, based on anhydrous zeolite plus metal.
53. The process of claim 44 wherein the anti-microbial powder has a second coating of a composition selected from the group consisting of silica, silicates, silicon dioxide, borosilicates, aluminosilicates, alumina, aluminum phosphate, zinc, zinc oxide, zinc silicate, copper, copper oxide, and mixtures thereof.
54. The process of claim 53 wherein the second coating comprises from about 0.1 to about 20% by weight, based on anhydrous zeolite plus metal.
55. The process of claim 44 wherein the antimicrobial powder is additionally coated with a dispersion enhancing coating selected from the group consisting of resin, hydrous metal oxide, and mixtures thereof.

- 36 56. The process of claim 44 wherein the antimicrobial powder has an average particle size less than about 10 microns.
57. The process of claim 44 wherein the antimicrobial powder has an average particle size less than about 6 microns.
58. The process of claim 44 wherein the antimicrobial powder has an average particle size greater than about 0.1 microns.
59. The process of claim 44 wherein the antimicrobial powder has an average particle size greater than about 0.2 microns.
- 5 60. The process of claim 44 wherein the polymer further comprises at least one additional component selected from the group consisting of defoamers, polymerization catalysts, stabilizers, delustering agents, whitening agents, pigments, fillers, plasticisers, ultraviolet absorbers, antioxidants, light stabilizers, ultraviolet stabilizers, processing stabilizers, and metal deactivators.
- 387 61. The process of claim 44 wherein the roll coater is a two-roll coater
62. The process of claim 44 wherein the polymer is applied by two or more coaters placed in series.
63. The process of claim 61 wherein the antimicrobial polymer coating is applied onto both opposed planar surfaces of the sheet metal.
64. The process of claim 61 wherein the polymer coating is at least partially hardened by a method selected from the group consisting of heat, infrared radiation, fluorescent radiation, ultraviolet radiation, gamma or beta radiation, X-ray radiation, or combinations thereof.
65. The process of claim 64 wherein cleaning comprises deoxidizing the surface by immersion in an acid solution, and rinsing in water.

66. The process of claim 61 wherein the metal sheet is made of a base metal material selected from the group consisting of aluminum, aluminum alloys, magnesium, and magnesium alloys.
67. The process of claim 61 wherein the metal sheet is stainless steel and wherein the coating has a thickness of from about 1 to about 30 microns.
68. The process of claim 61 wherein the coating after forming-processed is heated at a temperature of 100° to 300°C.
69. A metal sheet precoated with an antimicrobial polymer coating manufactured by the method of claim 1, 10, 20, 35 or 42.
70. A method of increasing stain resistance of a metal sheet by the method of claim 1, 10, 20, 35 or 42.
71. A method of increasing fingerprint resistance of a metal sheet by the method of claim 1, 10, 20, 35 or 42.

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